Original Paper

A novel method for the determination of Pb^{2+} based on the quenching of the fluorescence of CdTe quantum dots

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Abstract. A novel method for the determination of Pb^{2+} has been developed based on quenching of the fluorescence of thiol-capped CdTe quantum dots (QDs) by Pb^{2+} in aqueous solutions. Under optimum conditions, the relative fluorescence intensity was linearly proportional to the concentration of Pb^{2+} between 2.0×10^{-6} and $1.0 \times 10^{-4} \, mol \, L^{-1}$ with a detection limit of $2.7 \times 10^{-7} \, mol \, L^{-1}$. The relative standard deviation (RSD) was 4.6% for a $4.0 \times 10^{-5} \, mol \, L^{-1} \, Pb^{2+}$ solution ($N = 5$). As an application, the proposed method was successfully applied to the analysis of Pb^{2+} in food samples, and the results were satisfactory, i.e. consistent with those of flame atomic absorption spectrometry (FAAS).

Keywords: CdTe quantum dots; Pb^{2+}; quenching of the fluorescence; food samples

Lead is one of the most hazardous heavy metal elements, and it has been extensively studied due to its properties as a highly toxic cumulative poison in humans and animals. Sensitive analytical methods for Pb^{2+} determination are therefore of great interest. Up to now, a variety of methods have been developed for the determination of Pb^{2+}, including atomic absorption spectrometry [1, 2], anodic stripping voltammetry [3], spectrophotometry [4], and gas chromatography-mass spectrometry [5]. However, these methods all have their limits, such as high cost, robust sample handling, etc. So it is very important to develop simple, accurate and sensitive methods for the detection of Pb^{2+}.

Fluorescence quenching is a process that decreases the intensity of the fluorescence emission. It has been used to detect heavy metal ions in recent years [6]. Many organic dyes have been developed for the determination of heavy metal ions based on fluorescence quenching. However, for most organic dyes, the obvious disadvantages are their narrow excitation spectra, broad emission spectra and photobleaching. Quantum dots (QDs), with good optical and electrical properties, have attracted increasing attention in recent years [7–14]. Compared with organic dyes, QDs have a broad excitation spectrum, narrow and tunable emission spectrum, good photostability, chemical stability, and high brightness [15, 16]. Since CdS QDs were firstly reported as selective ion probes in aqueous samples [17, 18], many functionally capped luminescent QDs, such as CdS, CdSe and CdTe QDs, also showed a response to copper, silver and mercury ions [19–23]. Besides, thiol-capped CdTe QDs have been exploited in numerous applications, such as light-emitting devices [24], photonic [25] and biological labels [26]. However, to the best of our knowl-

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edge, little attention has been paid to the thiol-capped CdTe QDs used as Pb^{2+} probes. Therefore, research on Pb^{2+} determination based on fluorescence quenching of thiol-capped CdTe QDs is of current interest.

In this paper, a new approach has been proposed for the determination of Pb^{2+} based on fluorescence quenching of thiol-capped CdTe QDs. Some influencing factors, such as pH, ion concentration and foreign cations, were studied in detail. Under optimum conditions, the calibration graph was linear in the range of 2.0×10^{-6} to 1.0×10^{-4} mol L^{-1} of Pb^{2+} concentration, with a correlation coefficient of 0.997 and a detection limit of 2.7×10^{-7} mol L^{-1}. The proposed method was applied to the determination of Pb^{2+} in food samples, and the results were in good agreement with those of flame atomic absorption spectrometry (FAAS). In addition, the change of the thiol-capped CdTe QDs surface state played an important role in the quenching process.

Experimental

Apparatus

All fluorescence measurements were carried out with a Perkin-Elmer LS-55 fluorescence spectrometer (USA). Diluted solutions of CdTe QDs in aqueous medium were placed in a 1.0 cm quartz cuvette. The emission wavelength was fixed at 450–700 nm. The excitation wavelength was 383 nm, and the excitation slit and emission slit were 10.0 and 5.0 nm, respectively. The UV-Vis absorption spectra were recorded between 400 and 700 nm on a Thermo Nicolet Corporation Model evolution 300 (USA) with a 1.0 cm path-length quartz cuvette. FAAS was obtained with a TAS-990 spectrometer (Beijing, China). All pH measurements were carried out with a Mettler-Toledo GmbH MP120 pH Meter (Switzerland).

Chemicals

Tellurium powder (99.99%), CdCl$_2 \cdot$ 2.5H$_2$O (99.0%) and NaBH$_4$ (96%) were obtained from Tianjin Chemical Reagent Plant (Tianjin, China, http://www.reagent-1.com). Thioglycolic acid (TGA), Pb(NO$_3$)$_2$ (99%), KCl (99.8%), NaCl (99.5%), MgCl$_2$ (98%), AgNO$_3$ (99.8%), Cu(NO$_3$)$_2 \cdot$ H$_2$O (99%), NiSO$_4 \cdot$ 6H$_2$O (99%), MnSO$_4 \cdot$ H$_2$O (99%), ZnCl$_2$ (98%), CaCl$_2 \cdot$ 2H$_2$O (98%) and BaCl$_2 \cdot$ 2H$_2$O (99.5%) were obtained from Shanghai Chemical Reagent Co. Ltd. (Shanghai, China, http://www.scrcc1.online. sh.cn). All other chemicals were of analytical grade and were used without further purification. Double distilled water was used throughout the experiments.

Synthesis and purification of CdTe QDs

Thiol-capped CdTe QDs were synthesized according to the method reported by Zhang et al. [27] with some modifications. Briefly, fresh NaHTe solution was added to CdCl$_2$ solution in the presence of TGA in N$_2$ atmosphere, and the molar ratio of Cd^{2+}:Te^{2-}:TGA was fixed at 1:0.5:2.4. After mixing, the solution was heated to 100 °C

for 6 hours, and thiol-capped CdTe QDs could be obtained. The resulting products were precipitated by acetone, and superfluous TGA and Cd^{2+} that did not participate in the reaction were removed by centrifugation at 4000 rpm for 3 min. The process of purification had no obvious effect on the stability of the thiol-capped CdTe QDs, and the fluorescence intensity, peak width at half-height of CdTe QDs, showed no obvious changes after removing the redundant TGA. The resultant precipitate was re-dispersed in water, re-precipitated with an amount of acetone more than twice, and then kept at 4 °C in the dark for later use.

A 0.5 mL CdTe QDs was diluted with 2.0 mL phosphate-buffered saline (PBS) solution (pH = 9.0). Then the proper volume of the Pb^{2+} solution was added to a 5.0 mL tube, and the total volume of the mixed solution was made up to 5.0 mL with double distilled water. It should be mentioned that the fluorescence spectra were measured with the sample reacting for 10 min at room temperature to obtain a stable fluorescence intensity.

Sample preparation

The samples were decomposed by dry digestion in a muffle furnace. Solid samples were powdered and sieved through 200 mesh, then incinerated in porcelain crucibles until no smoke emerged and calcined at 520 °C for 7–8 hours in a muffle furnace. The cooled ashes were dissolved with 0.5 mol L^{-1} HNO$_3$ solutions and neutralized to pH = 7.0 with 0.1 mol L^{-1} NaOH solution [28].

Results and discussion

Characterization of as-prepared CdTe QDs

The particle sizes of CdTe QDs were determined from the first absorption maximum of the UV-Vis spectra using an empirical formula:

$$D = (9.8127 \times 10^{-7})\lambda^3 - (1.7147 \times 10^{-3})\lambda^2 + (1.0064)\lambda - 194.84$$

where D (nm) is the size of a given CdTe QD sample, and λ (nm) is the wavelength of the first excitonic absorption peak of the corresponding sample.

The concentrations of CdTe QDs were calculated using Lambert-Beer's law:

$$A = \varepsilon CL$$

In the above equations, A is the absorbance at the peak position of the first excitonic absorption peak for a given sample. C is the molar concentration (mol L^{-1}) of the CdTe QDs of the same sample. L is the path length (cm) of the radiation beam used for recording the absorption spectrum, and ε is the extinction coefficient per mole of CdTe QDs at the first exitonic absorption peak, which could be obtained with the formula $\varepsilon = 10043$ $(D)^{2.12}$ [29]. Figure 1 shows the UV-Vis absorption (a, c) and fluorescence (b, d) spectra of thiol-capped CdTe QDs. The UV-Vis absorption edge of CdTe QDs showed an obvious blue
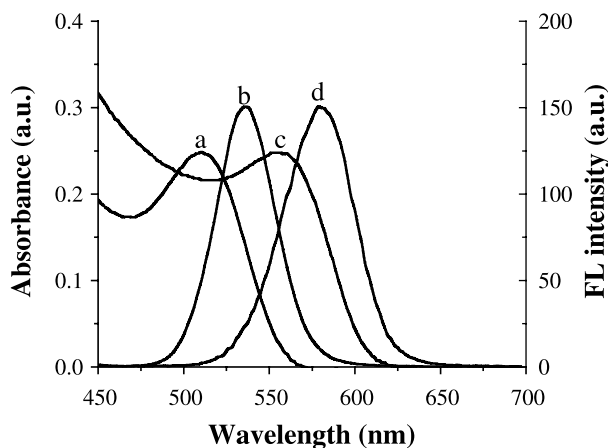
Fig. 1. UV-Vis absorption (*a*: 2.6 nm, *c*: 3.3 nm) and fluorescence (*b*: 2.6 nm, *d*: 3.3 nm) spectra of thiol-capped CdTe QDs
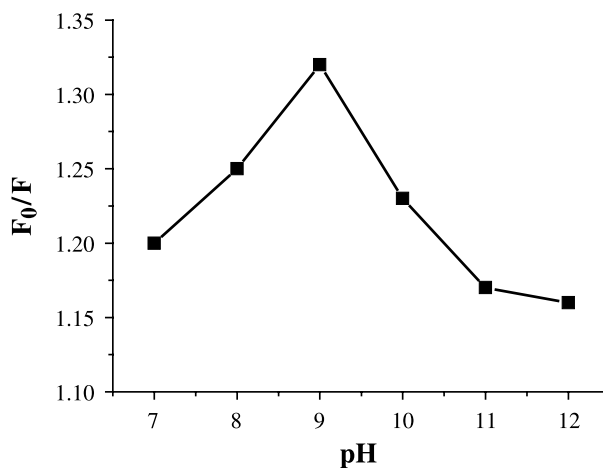

Fig. 2. Effect of pH on the reaction between CdTe QDs (3.3 nm) and Pb²⁺. The concentrations of CdTe QDs and Pb²⁺ were 3.83×10^{-8} and 4.0×10^{-5} mol L^{-1}, respectively

shift from the bulk band gap of 827 nm to 510 and 560 nm (Fig. 1a, c), indicating the effect of quantum confinement [30]. The sizes were 2.6 and 3.3 nm for 510 and 560 nm CdTe QDs at the first exitonic absorption peak, the concentrations of which were 3.08×10^{-5} mol L^{-1} (2.6 nm) and 2.87×10^{-5} mol L^{-1} (3.3 nm), respectively.

With an excitation wavelength of 383 nm, thiol-capped CdTe QDs exhibited an obvious, symmetrical fluorescence emission spectrum with an emission maximum at 536 and 582 nm, and without a tail on the right-hand side (Fig. 1b, d), indicating that the CdTe QDs have good fluorescence properties.

The quantum yield (QY) of as-prepared CdTe QDs was measured according to the method described in Ref. [31]. Rhodamin 6G, dissolved in anhydrous alcohol, was chosen as fluorescence standard (QY 95%). The QY of CdTe QDs was calculated by comparing with the integrated areas of emission between Rhodamin 6G and CdTe QDs. Experimental results supported that the fluorescence QY of CdTe QDs was 47.6% (2.6 nm) and 27.6% (3.3 nm), respectively.

Effect of pH

Previous reports suggested that solution acidity played an important role in the interaction of CdTe QDs with other molecules [32]. The effect of different pH buffer solutions on the fluorescence response of the interaction between CdTe QDs (3.3 nm) and Pb²⁺ was investigated using 0.1 mol L^{-1} PBS solutions in the range of pH 3.0 to 12.0 in our experiment. It was found that thiol-capped CdTe QDs synthesized under basic conditions showed extraordinarily weak fluorescence signals under acidic conditions, which is caused by its instability in acidic conditions. Further research showed that the fluorescence signals of the reaction between Pb²⁺ and CdTe QDs were also very weak. However, the fluorescence intensity of CdTe QDs decreased most severely in PBS 9.0 solution when the pH was between 7.0 and 12.0 (Fig. 2). With basicity rising, visible white precipitates emerged. Therefore, the former suitable reaction conditions in favor of an 0.1 mol L^{-1} pH 9.0 PBS solution were selected for further experiments.

Effect of different metal ions

Many metal ions have the potential to influence the QDs fluorescence emission. As shown in Table 1, several cations, including K⁺, Na⁺, Mn²⁺, Mg²⁺, Ba²⁺, Ca²⁺, Ni²⁺, Zn²⁺, Ag⁺, Cu²⁺ and Pb²⁺ had been selected to study the influence on the fluo-

Table 1. Effect of foreign cations on the fluorescence of CdTe QDs in pH 9.0 PBS solution. The concentration of Cu²⁺ and Ag⁺ were 1.0×10^{-6} mol L^{-1}, that of other ions was 1.0×10^{-5} mol L^{-1}

Metal ions	Contr.	K⁺	Na⁺	Mn²⁺	Mg²⁺	Ba²⁺	Ca²⁺	Ni²⁺	Zn²⁺	Cu²⁺	Ag⁺	Pb²⁺
F/F$_0$	1.00	0.97	1.01	0.98	0.94	0.96	0.98	0.87	0.96	0.12	0.03	0.40
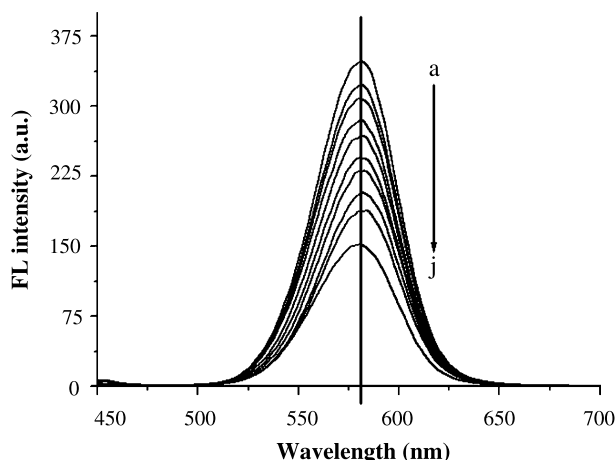
Fig. 3. Fluorescence emission spectra of thiol-capped CdTe QDs (3.3 nm) in addition of Pb^{2+} at pH 9.0 PBS solutions. The concentration of CdTe QDs was 3.83×10^{-8} mol L^{-1}; the Pb^{2+} concentrations were (*a*) 0, (*b*) 2.0, (*c*) 7.0, (*d*) 10.0, (*e*) 20.0, (*f*) 30.0, (*g*) 40.0, (*h*) 50.0, (*i*) 70.0, and (*j*) 100.0×10^{-6} mol L^{-1}. The excitation wavelength and emission maximum were 383 and 582 nm, respectively

rescence signals of thiol-capped CdTe QDs (3.3 nm) in our experiment. The results showed that Ag$^+$ and Cu^{2+} could strongly quench the fluorescence signals of CdTe QDs, as previously reported [19–23]. Among other cations, Pb^{2+} showed the strongest quenching of functionalized CdTe QDs fluorescence. Furthermore, the results proved that other cations slightly interfered with the sensitivity and selectivity of the Pb^{2+} determination.

Calibration curve and detection limit

Figure 3 shows the fluorescence emission spectra of thiol-capped CdTe QDs (3.3 nm) in the presence of Pb^{2+} at pH 9.0 in PBS solution. As shown in Fig. 3, with the addition of different concentrations of Pb^{2+} solutions, the fluorescence signals of CdTe QDs were quenched obviously, but without the emission peak shifting. It was found that Pb^{2+} ions quench the fluorescence intensity of CdTe QDs in a concentration dependence that is best described by a Stern-Volmer-type equation [33]:

$$F_0/F = 1 + Ksv[Pb^{2+}]$$

F_0 and F are the fluorescence intensity of the CdTe QDs in an ion-free solution and in the presence of Pb^{2+}, respectively. [Pb^{2+}] was the concentration of Pb^{2+}, and K_{SV} was found to be 1.3×10^4 L mol^{-1} of the 3.3 nm CdTe QDs in the equation. Under optimum conditions, for the CdTe QDs with a size of 3.3 nm, a

high linearity was observed in the Pb^{2+} concentration range from 2.0×10^{-6} to 1.0×10^{-4} mol L^{-1}. A correlation coefficient of 0.997 was acquired with a detection limit of 2.7×10^{-7} mol L^{-1}. The RSD was 4.6% for five repeating detection of 4×10^{-5} mol L^{-1} Pb^{2+} solutions.

Compared with the CdTe QDs of 3.3 nm, the Ksv was 9.23×10^3 mol L^{-1} for the 2.6 nm CdTe QDs, and the relative fluorescence intensity was linearly proportional to the concentration of Pb^{2+} between 1.0×10^{-6} and 6.0×10^{-5} mol L^{-1} with a detection limit of 2.3×10^{-7} mol L^{-1} for the CdTe QDs with a size of 2.6 nm. The RSD was 3.9% for a 4.0×10^{-5} mol L^{-1} Pb^{2+} solution ($N = 5$). The results showed that CdTe QDs of different sizes had similar detection limits and sensitivities.

Quenching the fluorescence of QDs may happen by energy transfer [34], charge diverting [35], and surface absorption [36], which may change the surface state of QDs. Previous studies on some inorganic cations, such as Cu^{2+}, Ag$^+$ and Hg^{2+} [19–23], revealed that some changes of the surface charges or components of QDs would change their photophysical properties.

In order to investigate the quenching mechanism of fluorescence by Pb^{2+}, UV-Vis absorption spectra of the interaction between CdTe QDs and Pb^{2+} were studied (Fig. 4). With the addition of Pb^{2+}, the excitonic peak became gentle, showing that the size of thiol-capped CdTe QDs had turned asymmetrical. Therefore, the process of quenching is static, and the surface state of thiol-capped CdTe QDs may be
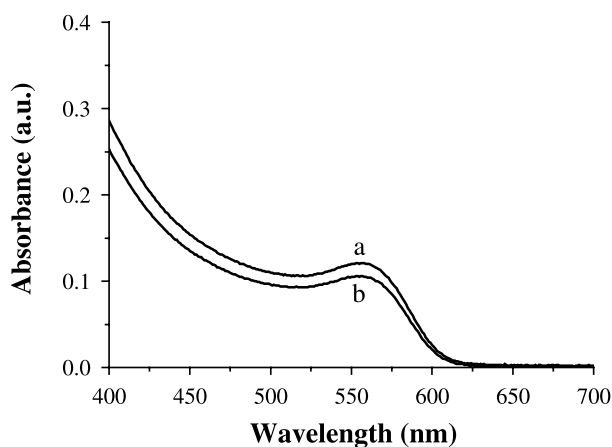
Fig. 4. UV-Vis absorption spectra of (*a*) thiol-capped CdTe QDs (3.3 nm) and (*b*) CdTe QDs + Pb^{2+} at pH 9.0 in PBS solution. The concentrations of CdTe QDs and Pb^{2+} were 7.2×10^{-5} and 8.3×10^{-5} mol L^{-1}, respectively

Table 2. Lineweaver-Burk equations based on static quenching in the system

CdTe QDs	Regression equations	Correlation coefficients
CdTe QDs (3.3 nm)	$(F_0 - F)^{-1} = 0.0030 + 2.38 \times 10^{-7} (C_{Pb}^{2+})^{-1}$	0.997
CdTe QDs (2.6 nm)	$(F_0 - F)^{-1} = 0.0036 + 8.16 \times 10^{-7} (C_{Pb}^{2+})^{-1}$	0.994

Table 3. Determination of Pb^{2+} in food samples with proposed method and FAAS

Sample	Proposed method (mg/kg)		FAAS (mg/kg)
	Average value (mg/kg)	RSD (%) ($N = 5$)	
Sample 1 (popcorn)	0.9583	4.2	1.0586
Sample 2 (instant noodles)	1.6473	4.0	1.8730

changed with the addition of Pb^{2+}, leading to the quenching of the fluorescence. Table 2 shows Lineweaver-Burk equations based on static quenching in the system. Good correlation coefficients can be obtained with Lineweaver-Burk equations, which further proves the static quenching mechanism.

Analytical application

The proposed method was applied to determine Pb^{2+} in food samples, such as popcorn (sample 1) and Instant Noodles (sample 2). Parallel measurements were carried out with five similar digested sample solutions by both the proposed method and FAAS. The results obtained by the proposed method were in good agreement with FAAS (results given in Table 3).

Conclusions

In summary, a novel method for the determination of Pb^{2+} is proposed based on the quenching of fluorescence of thiol-capped water-soluble CdTe QDs by Pb^{2+}. The fluorescence response was linearly proportional to the concentration of Pb^{2+} between 2.0×10^{-6} and 1.0×10^{-4} mol L^{-1}, with a detection limit of 2.7×10^{-7} mol L^{-1} for the CdTe QDs with a diameter of 3.3 nm. The 2.6 nm CdTe QDs have a similar detection limit and sensitivity under optimal conditions. The proposed method was successfully applied to the determination of Pb^{2+} in food samples and produced satisfactory results. The quenching mechanism of the fluorescence was possibly due to a change in the surface of the thiol-capped CdTe QDs induced by Pb^{2+}.

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